



IN THE MATTER OF an Application
for a French Patent

in the name of
RHODIA CHIMIE

filed under No. 98/15,160, and

IN THE MATTER OF an Application
for an Australian Patent.

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by RHODIA CHIMIE

in France on 27 November 1998

for "Organopolysiloxane compositions which cure to translucent elastomers from ambient temperature in the presence of moisture"

and the Official Certificate attached thereto.

Date: 11 April 2001

S. POTTS

Director

For and on behalf of RWS Group plc

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<p>Reserved for the INPI</p> <p>DATE OF SUBMISSION OF THE DOCUMENTS 27 NOV. 1998</p> <p>NATIONAL REGISTRATION 98/15.160</p> <p>DEPARTMENT OF FILING LY</p> <p>DATE OF FILING 27 NOV. 1998</p>		<p>1. NAME AND ADDRESS OF THE APPLICANT OR THE REPRESENTATIVE TO WHOM THE CORRESPONDENCE IS TO BE ADDRESSED</p> <p>TROLLIET Maurice RHODIA SERVICES Direction de la Propriété Industrielle CRIT-CARRIERES BP 62 69192 SAINT-FONS CEDEX</p>	
<p>2. APPLICATION</p> <p><input checked="" type="checkbox"/> patent <input type="checkbox"/> divisional application</p> <p><input type="checkbox"/> utility certificate <input type="checkbox"/> conversion of a European patent application <input type="checkbox"/> patent</p> <p>→ initial application</p>		<p>No. of permanent power of attorney</p> <p>11 February 98</p>	<p>Correspondent's references</p> <p>R 98170</p>
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<p>Title of the invention (maximum 200 characters)</p> <p>ORGANOPOLYSILOXANE COMPOSITIONS WHICH CURE TO TRANSLUCENT ELASTOMERS FROM AMBIENT TEMPERATURE IN THE PRESENCE OF MOISTURE</p>			
<p>3. APPLICANT(S)</p> <p>SIREN No.</p> <p>APE-NAF code</p> <p>Name and forenames (underline the surname) or company name</p> <p>RHODIA CHIMIE</p>		<p>Legal form</p> <p>S.A.</p>	
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<p>4. INVENTOR(S) The inventors are the applicants <input type="checkbox"/> yes <input checked="" type="checkbox"/> no If the answer is no, provide a separate designation</p>			
<p>5. REDUCTION OF THE RATE OF FEES <input type="checkbox"/> requested for the first time <input type="checkbox"/> requested prior to filing; attach copy of the favourable decision</p>			
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<p>8. SIGNATURE OF THE APPLICANT OR REPRESENTATIVE</p> <p>(name and capacity of the signatory - registration No.)</p> <p>(signature)</p> <p>TROLLIET Maurice</p>		<p>SIGNATURE OF THE RECEIVING OFFICIAL</p> <p>(signature)</p> <p>D. GIRAUD</p>	
		<p>SIGNATURE AFTER REGISTRATION OF THE APPLICATION AT THE INPI</p> <p>(illegible signature)</p>	

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(if the applicant is not the inventor or the sole inventor)

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NATIONAL REGISTRATION NO.

98/15.160

R 98170**TITLE OF THE INVENTION:**Organopolysiloxane compositions which cure to translucent elastomers
from ambient temperature in the presence of moisture**THE UNDERSIGNED****RHODIA CHIMIE****DESIGNATE(S) AS INVENTOR(S) (surname underlined, forenames, address):**1) DALBE Bernard

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NOTE: In exceptional cases, the name of the inventor may be followed by that of the company to which he belongs (membership company) when the latter is other than the company which is the applicant or proprietor.**Date and signature(s) of the applicant(s) or of the representative**

Saint-Fons, 19 January 1999

(signature)

Maurice TROLLIET

ORGANOPOLYSILOXANE COMPOSITIONS WHICH CURE TO
TRANSLUCENT ELASTOMERS FROM AMBIENT TEMPERATURE IN THE
PRESENCE OF MOISTURE

5 A subject-matter of the present invention is
single-component organopolysiloxane compositions which
are stable on storage in the absence of moisture and
which crosslink to adherent and translucent elastomers
in a thin layer (that is to say, within a thickness
10 range in particular from 0.3 to 3 mm), the crosslinking
being carried out from ambient temperature (that is to
say, within a temperature range from 5°C to 35°C) and
in the presence of moisture.

 It is known to prepare compositions having
15 these properties by blending mainly diorganopoly-
siloxane polymer(s) comprising end alkoxy groups,
inorganic filler(s) not generating opaqueness, silanes
substituted by specific hydrolysable groups, agent(s)
for improving adhesion and a curing (or crosslinking)
20 catalyst.

 Compositions of this type figure more
especially in US-A-5 674 936 and US-A-5 698 653. The
compositions in accordance with this prior art are
formed by blending a diorganopolysiloxane polymer
25 comprising end alkoxy groups, a siliceous inorganic
filler, a nonreactive diorganopolysiloxane polymer
comprising end trialkylsiloxyl groups, a curing

catalyst based on a tetraalkyl titanate and an agent for improving the adhesion consisting of a 1,3,5-tris(trialkoxysilyl)alkyl isocyanurate (in the case of US-A-5 674 936) or of an epoxidized silane (in 5 the case of US-A-5 698 653).

The compositions in accordance with this prior art necessarily require the use, from the start, of an already functionalized diorganopolysiloxane polymer (comprising at least two alkoxyl groups at each 10 chain end), which is obtained by reacting, in a separate preliminary stage, a tri- or a tetraalkoxy-silane with a diorganopolysiloxane polymer comprising a hydroxyl group at each chain end in the presence of a catalyst. The compositions in accordance with this 15 prior art necessarily also require the use of an agent for improving the adhesion.

An aim of the present invention is to provide novel single-component organopolysiloxane compositions which are obtained by starting directly from 20 organopolysiloxane polymers comprising hydroxyl groups in their structures.

Another aim of the present invention is to provide single-component organopolysiloxane compositions of this type which will undergo in situ, 25 during their preparation, a reaction for complete functionalization or functionalization which is as close as possible to the maximum degree of

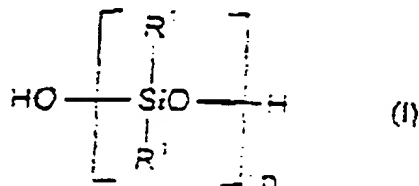
functionalization accessible and will exhibit, for this reason, a high level of stability on storage in cartons.

Yet another aim of the present invention is
5 to provide single-component organopolysiloxane compositions which do not necessarily resort to the use of an agent for improving the adhesion and which make it possible to obtain, without use of such an agent, translucent elastomers with very good adhesion to
10 various substrates, in particular plastics, such as, for example, poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA).

Yet another aim of the present invention is to provide single-component organopolysiloxane
15 compositions which can be prepared by using, without distinction, a batchwise mode or a continuous mode.

The discovery has thus been made, and it is this which forms the subject-matter of the present invention, of single-component organopolysiloxane
20 compositions which are stable on storage in the absence of moisture and which crosslink to translucent and adherent elastomers in the presence of moisture, characterized in that they are capable of being obtained by carrying out, in a single closed reactor
25 with stirring, operating according to a batchwise mode or a continuous mode, successive stages 1 to 3 defined below:

- stage 1: functionalization stage, during which:
 - (i) at least one reactive linear diorganopolysiloxane A comprising a hydroxyl group at each chain end, of formula:



5

in which:

- the R^1 substituents, which are identical or different, each represent an aliphatic, cyclanic or aromatic, saturated or unsaturated, substituted or unsubstituted, C_1 to C_{13} monovalent hydrocarbonaceous radical;
- n has a value sufficient to confer, on the diorganopolysiloxanes of formula (I), a dynamic viscosity at 25°C ranging from 1 000 to 1 000 000 mPa.s;

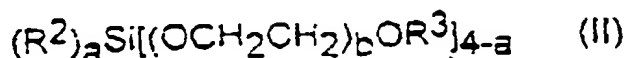
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- (2i) and at least one hydroxylated organopolysiloxane resin B exhibiting, in its structure, at least two different units chosen from those of formulae $(\text{R}^1)_3\text{SiO}_{1/2}$ (M unit), $(\text{R}^1)_2\text{SiO}_{2/2}$ (D unit), $\text{R}^1\text{SiO}_{3/2}$ (T unit) and SiO_2 (Q unit), at least one of these units being a T or Q unit and the R^1 radicals, which are identical or different, having the meanings given above with respect to the formula (I), the said resin

20

having a content by weight of hydroxyl group
ranging from 0.1 to 10%;

(3i) are reacted with at least one polyalkoxysilane C
of formula:



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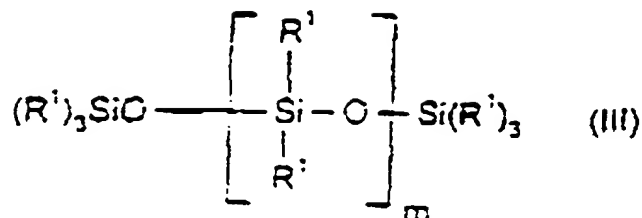
in which:

- the R^2 substituent represents an aliphatic,
cyclanic or aromatic, saturated or
unsaturated, substituted or unsubstituted, C_1
10 to C_{13} monovalent hydrocarbonaceous radical;
- the R^3 symbols, which are identical or
different, each represent a linear or
branched C_1 to C_8 alkyl radical;
- a is zero or 1;
- 15 - b represents zero or 1;

(4i) the reaction of (i) and (2i) with (3i) being
carried out in the presence of a catalytically
effective amount of a functionalization catalyst
D, with the exception of the use of an organic
20 titanium derivative;

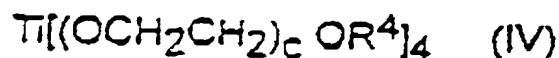
(5i) it being possible for the reaction medium of
stage 1 additionally to comprise:

- + at least one aliphatic C_1 to C_3 alcohol ϵ ; and/or
- + at least one nonreactive linear diorganopoly-
25 siloxane F of formula:



in which:

- the R^1 substituents, which are identical or different, have the same meanings as those given above for the reactive diorganopolysiloxane A of formula (I);
- m has a value sufficient to confer, on the polymers of formula (III), a dynamic viscosity at 25°C ranging from 10 to 200 000 mPa·s;
- stage 2: blending (or compounding) stage, during which:
 - (6i) an inorganic filler G based on amorphous silica in the form of a solid;
 - (7i) an effective amount of a curing catalyst H comprising at least one organic titanium derivative chosen from the group consisting of:
 - + H1 monomers of formula:



in which:

- the R^4 substituents, which are identical or different, each represent a linear or branched C_1 to C_{12} alkyl radical;
- c represents zero, 1 or 2;

- with the conditions according to which, when the c symbol represents zero, the R⁴ alkyl radical has from 2 to 12 carbon atoms and, when the c symbol represents 1 or 2, the R⁴ alkyl radical has from 1 to 4 carbon atoms;
- 5 + H₂ polymers resulting from the partial hydrolysis of the monomers of formula (IV) in which the R⁴ symbol has the abovementioned meaning with the c symbol representing zero;
- 10 (8i) optionally at least one nonreactive linear diorganopolysiloxane F corresponding to the formula (III) mentioned above; and
- (9i) optionally at least one auxiliary agent I known to a person skilled in the art, which is
- 15 generally chosen, when it is needed, according to the applications in which the compositions according to the present invention are employed; are introduced in any order into the functionalization medium of stage 1, which is kept stirred;
- 20 • stage 3: finishing stage, during which the base blend obtained, kept stirred, is subjected to a devolatilization operation carried out under a pressure below atmospheric pressure.

In accordance with a preferred arrangement of

25 the invention, the following are used to prepare the single-component organopolysiloxane compositions, on

the basis of 100 parts by weight of hydroxylated linear diorganopolysiloxane(s) A:

- from 3 to 30 parts of hydroxlyated resin(s) B,
- from 2 to 15 parts of polyalkoxysilane(s) C,
- 5 - a catalytically effective amount of functionalization catalyst D,
- from 0 to 2 parts of alcohol(s) E,
- from 0 to 30 parts of nonreactive linear diorgano-polysiloxane(s) F,
- 10 - from 2 to 40 parts of siliceous filler G,
- from 0.3 to 5 parts of organic titanium derivative(s) H, and
- from 0 to 20 parts of auxiliary agent(s) I.

In accordance with a more preferred arrangement of
15 the invention, the following are used to prepare the single-component organopolysiloxane compositions, on the basis of 100 parts by weight of hydroxylated linear diorganopolysiloxane(s) A:

- from 5 to 15 parts of hydroxlyated resin(s) B,
- 20 - from 3.5 to 7 parts of polyalkoxysilane(s) C,
- a catalytically effective amount of functionalization catalyst D,
- from 0 to 1 part of alcohol(s) E,
- from 5 to 20 parts of nonreactive linear diorgano-
- 25 polysiloxane(s) F,
- from 8 to 20 parts of siliceous filler G,

- from 0.5 to 3 parts of organic titanium derivative(s)
H. and
- from 0 to 20 parts of auxiliary agent(s) I.

The R¹ substituents mentioned above for the
5 organopolysiloxane polymers A and F (optional)
comprise:

- alkyl and haloalkyl radicals having from 1 to 13
carbon atoms, such as the methyl, ethyl, propyl,
isopropyl, butyl, pentyl, hexyl, 2-ethylhexyl, octyl,
10 decyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl or
4,4,4,3,3-pentafluorobutyl radicals,
- cycloalkyl and halocycloalkyl radicals having from 5
to 13 carbon atoms, such as the cyclopentyl,
cyclohexyl, methylcyclohexyl, propylcyclohexyl,
15 2,3-difluorocyclobutyl or 3,4-difluoro-5-methyl-
cycloheptyl radicals,
- alkenyl radicals having from 2 to 8 carbon atoms,
such as the vinyl, allyl or 2-butenyl radicals,
- mononuclear aryl and haloaryl radicals having from 6
20 to 13 carbon atoms, such as the phenyl, tolyl, xylyl,
chlorophenyl, dichlorophenyl or trichlorophenyl
radicals,
- cyanoalkyl radicals in which the alkyl linkages have
from 2 to 3 carbon atoms, such as the β -cyanoethyl
25 and γ -cyanopropyl radicals.

Mention may be made, as concrete examples of
(R¹)₂SiO_{2/2} or (R¹)₂SiO units present in the hydroxylated

diorganopolysiloxanes A of formula (I) and in the optional nonreactive diorganopolysiloxanes F of formula (III), of:

- (CH₃)₂SiO,
- 5 CH₃(CH₂=CH)SiO,
- CH₃(C₆H₅)SiO,
- (C₆H₅)₂SiO,
- CF₃CH₂CH₂(CH₃)SiO,
- NC-CH₂CH₂(CH₃)SiO,
- 10 NC-CH(CH₃)CH₂(CH₂=CH)SiO,
- NC-CH₂CH₂CH₂(C₆H₅)SiO.

It must be understood that, in the context of the present invention, use may be made, as hydroxylated polymers A of formula (I), of a blend composed of
15 several hydroxylated polymers which differ from one another in the value of the viscosity and/or the nature of the substituents bonded to the silicon atoms. It must furthermore be pointed out that the hydroxylated polymers A of formula (I) can optionally comprise T
20 units of formula R¹SiO_{3/2} and/or SiO₂ units in the proportion of at most 1% (these % values expressing the number of T and/or Q units per 100 silicon atoms). The same comments apply to the (optional) nonreactive polymers F of formula (III).

25 The R¹ substituents of the hydroxylated polymers A and of the (optional) nonreactive polymers F advantageously used, because of their availability in

industrial products, are the methyl, ethyl, propyl, isopropyl, n-hexyl, phenyl, vinyl and 3,3,3-trifluoropropyl radicals. More advantageously, at least 80% by number of these substituents are methyl radicals.

- 5 Use is made of hydroxylated polymers A having a dynamic viscosity at 25°C ranging from 1 000 to 1 000 000 mPa·s and preferably ranging from 10 000 to 200 000 mPa·s.

- 10 As regards the (optional) nonreactive polymers F, they exhibit a dynamic viscosity at 25°C ranging from 10 to 200 000 mPa·s and preferably ranging from 50 to 150 000 mPa·s.

- 15 The nonreactive polymers F, when they are used, can be introduced either entirely in the reaction medium of stage 1 or entirely in the reaction medium of stage 2 or simultaneously in both these media; in the latter case, the fraction of constituent F introduced in the medium of stage 1 may be identical to or different from (in terms of nature and/or of proportions of the constituent in each fraction) the fraction of constituent F also introduced in the medium of stage 2. Preferably, the constituent F is introduced entirely in the reaction medium of stage 1.

- 20 Mention may be made, as examples of R^1 substituents of the hydroxylated organopolysiloxane resins B which are suitable or which are advantageously used, of the various R^1 radicals of this type

particularly mentioned above for the hydroxylated polymers A and the (optional) nonreactive polymers F. These silicone resins are well known branched organopolysiloxane polymers, the processes for the preparation of which are disclosed in numerous patents. 5 Mention may be made, as concrete examples of resins which can be used, of the MQ, MDQ, TD and MDT resins.

Mention may preferably be made, as examples of resins which can be used, of the hydroxylated organopolysiloxane resins B not comprising a Q unit in 10 their structures. Mention may more preferably be made, as examples of resins which can be used, of the hydroxylated TD and MDT resins comprising at least 20% by weight of T units and having a content by weight of hydroxyl group ranging from 0.3 to 5%. Even more 15 preferably, use is made of resins of this type in the structures of which at least 80% by number of the R^1 substituents are methyl radicals. The hydroxyl groups of the B resins can be carried by the M, D and/or T 20 units.

As regards the polyalkoxysilanes C of formula (II), mention may be made, as concrete examples of R^2 substituents which are suitable or which are advantageously used, of the same radicals as those 25 particularly mentioned above for the R^1 substituents of the hydroxylated polymers A and of the nonreactive polymers F. Mention may be made, as examples of R^3

radicals, of C₁ to C₄ alkyl radicals, such as the methyl, ethyl, propyl, isopropyl and n-butyl radicals.

Mention may in particular be made, among the polyalkoxysilanes C of formula (III) which are used in the context of the present invention, of those listed below:

- Si(OCH₃)₄
- Si(OCH₂CH₃)₄
- Si(OCH₂CH₂CH₃)₄
- 10 (CH₃O)₃SiCH₃
- (C₂H₅O)₃SiCH₃
- (CH₃O)₃Si(CH=CH₂)
- (C₂H₅O)₃Si(CH=CH₂)
- (CH₃O)₃Si(CH₂-CH=CH₂)
- 15 (CH₃O)₃Si[CH₂-(CH₃)C=CH₂]
- (C₂H₅O)₃Si(OCH₃)
- Si(OCH₂-CH₂-OCH₃)₄
- CH₃Si(OCH₂-CH₂-OCH₃)₃
- (CH₂=CH)Si(OCH₂CH₂OCH₃)₃
- 20 C₆H₅Si(OCH₃)₃
- C₆H₅Si(OCH₂-CH₂-OCH₃)₃.

The polyalkoxysilanes C of formula (III) preferably used are: Si(OC₂H₅)₄, CH₃Si(OCH₃)₃, CH₃Si(OC₂H₅)₃, (C₂H₅O)₃Si(OCH₃), (CH₂=CH)Si(OCH₃)₃ and

25 (CH₂=CH)Si(OC₂H₅)₃.

As regards the functionalization catalyst D, in the presence of which the reaction of the

hydroxylated polymers A and of the hydroxylated resins B with the polyalkoxysilanes C takes place, recourse may be had in particular to the following compounds:

- potassium acetate (cf. US-A-3 504 051),
- 5 - various inorganic oxides (cf. FR-A-1 495 011),
- carbamates (cf. EP-A-0 210 402),
- lithium hydroxide (cf. EP-A-0 367 696),
- sodium hydroxide or potassium hydroxide (cf. EP-A-0 457 693).

- 10 In the context of the present invention, the use is recommended, as catalyst D, of lithium hydroxide of formula LiOH or LiOH·H₂O. It is preferably used in solution in at least one aliphatic alcohol E having from 1 to 3 carbon atoms, such as, for example,
- 15 methanol, ethanol, isopropanol or a mixture of these alcohols. When one (or several) alcohol(s) is(are) present in the reaction medium, the amount employed lies within the range from 0.1 to 2 parts by weight and preferably from 0.2 to 1 part by weight per 100 parts
- 20 of hydroxylated polymer(s) A.

- The term "catalytically effective amount of catalyst D" is understood to mean an amount such that the functionalization reaction rate is as high as possible, in particular on using Si(OC₂H₅)₄,
- 25 CH₃Si(OCH₃)₃, CH₃Si(OC₂H₅)₃, (C₂H₅O)₃Si(OCH₃), (CH₂=CH)Si(OCH₃)₃ and (CH₂=CH)Si(OC₂H₅)₃ as functionalization agent. In the majority of cases, use is made of

0.001 to 5 mol of catalyst per 1 mol of silanol groups ($\equiv\text{Si-OH}$) contributed, first, by the hydroxylated polymer(s) A and, secondly, [lacuna] the hydroxylated resin(s) B. In the preferred case, in which lithium hydroxide is resorted to, use is made of 0.005 to 0.5 mol of LiOH per 1 mol of silanol groups.

As indicated above, the inorganic filler G is composed of amorphous silica in the form of a solid. The physical state in which the silica is provided is immaterial, that is to say that the said filler can be provided in the form of a powder, micropearls, granules or beads, provided that this filler is sufficiently dispersed within the compositions according to the present invention to achieve the desired objective of translucency.

Any precipitated silica or pyrogenic silica (or fumed silica) known to a person skilled in the art is suitable as amorphous silica capable of being employed in the invention. Of course, composites of different silicas can also be used.

Preference is given to precipitated silicas in the powder form, fumed silicas in the powder form, or their mixtures; their BET specific surface area is generally greater than $40 \text{ m}^2/\text{g}$ and preferably between 100 and $300 \text{ m}^2/\text{g}$; use is more preferably made of fumed silicas in the powder form.

These fillers may have been surface-modified by treatment with the various organosilicon compounds customarily employed for this use. Thus, these organosilicon compounds can be organochlorosilanes, diorgano-
5 cyclopolysiloxanes, hexaorganodisiloxanes or hexaorganodisilazanes (cf. FR-A-1 126 884, FR-A-1 136 885 and FR-A-1 236 005). The treated fillers include, in the majority of cases, from 2 to 20% of their weight of organosilicon compounds.

10 As regards the curing catalyst H, mention may be made, as examples of R^4 symbols in the organic titanium derivatives H1 of formula (IV), of the radicals: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, hexyl, 2-ethylhexyl, octyl, decyl and
15 dodecyl.

Mention may be made, as concrete examples of H1 monomers of formula (IV), of: ethyl titanate, propyl titanate, isopropyl titanate, butyl titanate, 2-ethylhexyl titanate, octyl titanate, decyl titanate, dodecyl
20 titanate, β -methoxyethyl titanate, β -ethoxyethyl titanate, β -propoxyethyl titanate or the titanate of formula $Ti[(OCH_2CH_2)_2OCH_3]_4$. Mention may be made, as concrete examples of H2 polymers originally from the partial hydrolysis of titanate monomers, of: the H2
25 polymers originating from the partial hydrolysis of isopropyl, butyl or 2-ethylhexyl titanates.

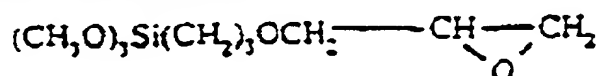
In carrying out the invention, use is preferably made, as curing catalyst, of the following H1 monomer titanates, taken alone or as a mixture: ethyl titanate, propyl titanate, isopropyl titanate or
5 butyl (n-butyl) titanate.

The single-component organopolysiloxane compositions according to the present invention can additionally comprise one or more auxiliary agent(s) I such as in particular, per 100 parts by weight of
10 hydroxylated linear diorganopolysiloxane polymer(s) A:
- optionally from 0.1 to 10 parts of an adhesion promoter I1,
- optionally an effective amount of at least one compound taken from the group formed by antifungals
15 I2, bactericides I3, inert organic diluents I4 (such as, for example: toluene, xylene, heptane, white spirit, trichloroethylene or tetrachloroethylene), plasticizers I5 belonging, for example, to the group of the alkylbenzenes with a molecular weight of
20 greater than 200 g/mol comprising a branched or unbranched alkyl residue having from 10 to 30 carbon atoms, and thixotropic agents I6.

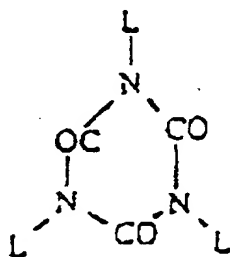
The adhesion promoter I1, when one of them is used, is preferably chosen from organosilicon compounds
25 carrying both (1) hydrolysable groups bonded to the silicon atom and (2) organic groups substituted by the

radicals chosen from the group of the isocyanato, epoxy, alkenyl and isocyanurate radicals.

Mention may be made, as illustration, of the organosilicon compounds corresponding to the formulae below (accompanied by the numbers of the patents in which they are disclosed):



US-A-4 115 356



where $L = -(\text{CH}_2)_3\text{-Si}(\text{OCH}_3)_3$

US-A-3 517 001

The single-component organopolysiloxane compositions in accordance with the present invention are prepared with moisture excluded by carrying out the preparation in a closed reactor, equipped with a stirrer, in which, if need be, a vacuum can be applied and then the air driven off can optionally be replaced by an anhydrous inert gas, for example by nitrogen.

For this preparation, it is recommended to use an installation, operating according to a batchwise mode or a continuous mode, which makes it possible:

- to intimately stir, with moisture excluded: in stage 1, the constituents A, B, C, D, E (optional) and F (optional); then, in stage 2, the reaction mixture from stage 1 made up by the addition of the constituents G, H, F (optional) and I (optional); and
- to discharge, in stage 3, the volatile materials present (low molecular weight polymers, alcohol formed during the functionalization reaction, alcohol E optionally used).

10 Mention may be made, as examples of installations, of: slow dispersers, paddle, propeller, arm or anchor mixers, planetary mixers, hook mixers, or single-screw or multiple-screw extruders.

 Each of the stages employed in this
15 preparation is carried out at a temperature lying within the range from 10 to 110°C. Preferably, each of the stages is carried out at a temperature ranging from 15 to 90°C.

 Stage 1 is carried out for a sufficient
20 period of time (ranging, for example, from 10 seconds to 10 minutes) to carry out a reaction for complete functionalization or functionalization which is as close as possible to the maximum degree of functionalization accessible under the operating
25 conditions chosen.

Stage 2 is carried out for a sufficient period of time (ranging, for example, from 10 seconds to 30 minutes) to arrive at homogeneous compositions.

Stage 3 is generally carried out under a reduced pressure of between 20×10^2 Pa and 900×10^2 Pa for a sufficient period of time (ranging, for example, from 10 seconds to 1 hour) to discharge all the volatile materials.

The compositions in accordance with the invention are stable on storage in the absence of water, curing from ambient temperature in the presence of moisture. The curing (or the crosslinking) takes place from the exterior toward the interior of the body of the compositions. First a surface skin is formed and then the crosslinking continues into the body.

They can be employed in multiple applications, such as pointing in the construction industry, or the assembling and adhesive bonding of the most diverse materials (metals; plastics, such as, for example, PVC or PMMA; natural and synthetic rubbers; wood; board; earthenware; brick; glass; stone; concrete; masonry components), both in the context of the construction industry and in that of the automobile, domestic electrical appliance and electronics industries.

The compositions in accordance with the invention result, after curing, in translucent

elastomers which have very good adhesion to various substrates and which furthermore exhibit the advantage, first, of not yellowing over time under the oxidizing action of the air and, secondly, of not being corrosive with respect to metals or metal alloys, such as, for example, aluminum, steel, copper or bronze, with which they are in contact or to which they adhere.

The following examples illustrate the invention without limiting its scope thereof.

10

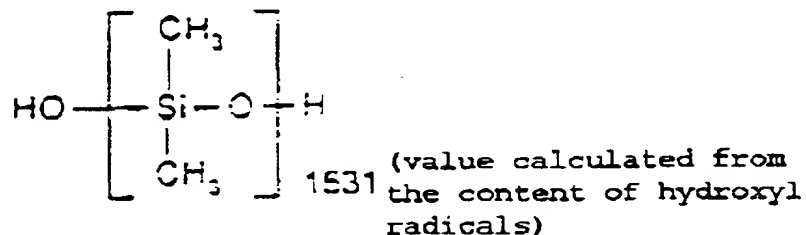
EXAMPLE 1

Composition prepared according to a batchwise mode.

Stage 1: the following are introduced into a 2 liter mixer equipped with a three-bladed stirrer of butterfly type:

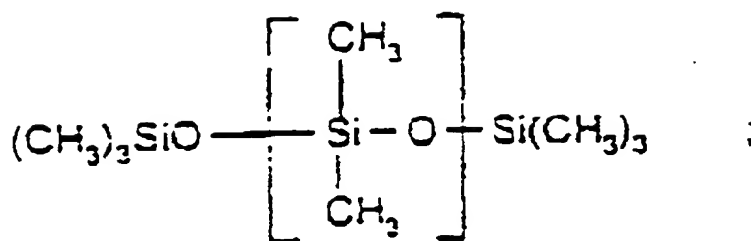
- 670 g of an α,ω -dihydroxypolydimethylsiloxane silicone oil A with a viscosity of 135 000 mPa.s at 25°C having 0.03% by weight of hydroxyl radicals (i.e. 0.2 g of OH radicals); this polyorganosiloxane

20 A has the mean formula:



- 90 g of an α,ω -di(trimethylsiloxyl)polydimethylsiloxane oil F with a viscosity of 1 000 mPa.s at 25°C; this polyorganosiloxane F has the mean formula:

22



approximately 180

- and 90 g of hydroxylated organopolysiloxane resin B
 of MDT type having 1% by weight of hydroxyl radicals
 5 (i.e. 0.9 g of OH radicals) and composed of: 4% by
 weight of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units, 71% by weight of
 $(\text{CH}_3)_2\text{SiO}_{2/2}$ units and 25% by weight of $\text{CH}_3\text{SiO}_{3/2}$ units;
 this resin exhibits a viscosity of 100 mPa·s at 25°C.

The introduction takes place in the order
 10 indicated above, the operation being carried out at
 ambient temperature (23°C). Once the introduction is
 complete, the contents of the mixer are stirred at
 200 revolutions/minute for 4 minutes.

At the end of this period, 30 g of vinyltri-
 15 methoxysilane C are added; the contents of the mixer
 are subsequently stirred at 200 revolutions/minute for
 2 minutes.

At the end of this period, 4 g of a 4% by
 weight solution of lithium hydroxide ($\text{LiOH}\cdot\text{H}_2\text{O}$) in
 20 methanol (i.e. 0.16 g of lithium hydroxide $\text{LiOH}\cdot\text{H}_2\text{O}$ D
 and 3.84 g of methanol E) are introduced into the mixer
 and the mixture is left to react with stirring at
 200 revolutions/minute for 2 minutes.

During stage 1, the temperature of the reaction mass varied within a region ranging from 23°C to 30°C.

Stage 2: at the end of the abovementioned
5 period, 100 g of fumed silica G, sold by Degussa under the trade name Aerosil 200 with a specific surface area of 200 m²/g and treated with octamethylcyclotetra-
siloxane, this treatment agent representing approxi-
mately 6% of the weight of the treated filler, are
10 introduced at ambient temperature (23°C); this treated silica is introduced gradually, with variable stirring, over a period of time of 18 minutes; once the introduction is complete, the contents of the mixer are subsequently stirred at 400 revolutions/minute for
15 4 minutes.

At the end of this period, 13 g of n-butyl titanate H1 are introduced and the contents of the mixer are stirred at 400 revolutions/minute for 4 minutes.

20 During stage 2, the temperature of the reaction mass rose until the value 75°C was reached.

Stage 3: at the end of the abovementioned period, the contents of the mixer are again stirred at 150 revolutions/minute at the temperature at which they
25 are found (approximately 75°C) for 6 minutes, the operation being carried out this time at a pressure below atmospheric pressure, of the order of 40×10^2 Pa,

and then they are packaged in a container which is
leaktight to atmospheric moisture and to water vapor.

A single-component composition is obtained
which has the appearance of a homogeneous, translucent
5 and sticky paste.

The various desired properties mentioned
below are measured:

1. Applicational properties:

• Tack-free time:

10 This is a measurement of the surface cross-
linking time of the composition at 23°C and at a
relative humidity of 50%. This tack-free time can
generally be correlated with several parameters which
are important for the user, such as, in particular, the
15 time at the end of which the surface of the composition
is not deformed under the effect of a slight contact
with a finger or else no longer "picks up" the dust
present in the surrounding air.

This measurement is made according to the
20 directions of the ASTM Standard C 679-87 (revised in
1992), using a "rectangular mass" of 17 g instead of
30 g.

• Yellowing index:

A composition fraction is spread with a
25 doctor blade over a surface, so as to produce a film
with a thickness of 2 mm. The film is left to crosslink
for 7 days at 23°C and at a relative humidity of 50%.

The film, thus crosslinked, is subsequently introduced into an oven at 100°C for 7 days.

A spectrophotometer sold by ACS under the reference Spectro Sensor II is used to make the
5 measurement of yellowing index.

The crosslinked film, after its stay in the study, is placed on the spectrophotometer. It is examined under reflection with the "illuminant C" feature (which represents the radiation of average
10 daylight) and while using a large aperture (10° angle). Under these conditions, a yellowing index can be calculated; it is the Yellowing Index (1925), defined in the following way:

$$\text{Yellowing Index (1925)} = \frac{128 \times X - 106 \times Z}{Y}$$

15 where X, Y and Z are the trichromatic values of the CIE (Commission Internationale de l'Eclairage [International Commission on Illumination]). The lower the index, the less yellow the sample.

• Transparency index:

20 Another composition fraction is spread with a doctor blade over a contrast card (sold by Erichsen GmbH under the reference 2415) so as to produce a film with a thickness of 2 mm. The film is left to crosslink for 7 days at 23°C and at a relative humidity of 50%.

25 The spectrophotometer described above with respect to the measurement of yellowing index is used to measure the transparency index.

The "transparency" mode is adopted and two measurements are made: first on the white part of the contrast card and then on the black part of the latter. The measurements are made under reflection with the "illuminant C" feature with an aperture with an angle of 10° . The transparency index is calculated by producing the ratio of the Y black background/Y white background values.

2. Properties of adhesion to PVC (poly(vinyl chloride)):

The self-adhesiveness of the composition is evaluated by depositing, from another composition fraction, two strips with a thickness of approximately 5 mm on various PVC substrates. The length of each substrate, corresponding to the length of each strip deposited, is approximately 75 mm.

Two cases can be presented:

- either the PVC substrate is covered with a plastic film: in this case, the said film is removed and the two composition strips are immediately deposited;
- or the PVC substrate is not covered with a plastic film: in this case, the PVC substrate is cleaned with a dry rag prior to the application of the two composition strips.

The strips are subsequently left to crosslink for 7 days at 23°C and at 50% relative humidity.

The substrates supporting the strips are then immersed for 4 days at 23°C in a bath of distilled water at 23°C. The substrates are subsequently removed from the bath and are left to dry at 23°C for 24 hours before carrying out the adhesion test by peeling.

This test is carried out in the following way:

- + the end of one of the strips is separated over approximately 10 mm using a razor blade;
- 10 + the strip is positioned at an angle of 120° with respect to the plane of the substrate;
- + a pull is exerted with the hand which makes it possible to detach or to tear off the strip over approximately 50 mm;
- 15 + the operation is repeated with respect to the second strip;
- + the blanks which had adhered to the substrate are subsequently examined.

If there is no residual composition film at the surface of the substrate, failure is said to be adhesive. The composition does not adhere to the PVC substrate: (-) will be recorded in the table of the corresponding results.

If a continuous composition film remains at the surface of the substrate, failure is said to be cohesive. The composition adheres well to the PVC

substrate: (+) will be recorded in the table of the results.

3. Mechanical properties:

A film with a thickness of 2 mm is spread using a doctor blade, starting from another fraction of the composition to be evaluated.

In the case where it is desired to make measurements over a thickness of 6 mm, another fraction of the composition is spread in a groove with a thickness of 6 mm and a width of 20 mm. Leveling is carried out using a spatula.

In all cases, the composition is left to crosslink for 7 days at 23°C and at 50% relative humidity.

The following properties are measured on the crosslinked products:

a) Shore A Hardness:

The measurements are made on the face of the composition which has crosslinked in contact with the air. For the 6 mm film, the measurement is made over one thickness, whereas, for the 2 mm film, the measurement is made by superimposing 3 thicknesses of films.

The measurements are made according to the directions of Standard ASTM-D-2240.

b) Mechanical properties on the 2 mm film:

Test specimens of H2 type are prepared and the measurements are made according to the directions of Standard AFNOR-T-46002.

5 The following values are recorded:

- tensile strength (in MPa), reported as T/S;
- elongation at break (in %), reported as E/B;
- modulus at 100% elongation (in MPa), reported as M100.

10 The results are collated in Table I, given below.

EXAMPLE 2

Composition prepared according to a continuous mode.

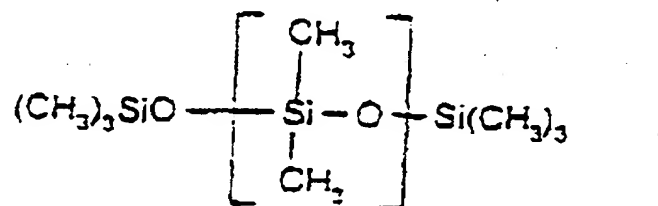
15 The composition is prepared according to a continuous mode by carrying out the preparation in a twin-screw extruder manufactured by Werner-Pfleiderer. The screws have a diameter of 58 mm and a length of 192 cm.

20 The rotational speed of the screws is set at 500 revolutions/minute.

 This extruder is equipped with 8 zones for regulating the temperature of the barrel, each zone having a length of 24 cm. The zones 1 to 8 of the
25 barrel are all subjected to cooling by circulation of water at 15°C.

Stage 1: the following are introduced into zone No. 1 of the extruder, the introduction being carried out at ambient temperature (23°C):

- 53 kg/hour of α,ω -dihydroxypolydimethylsiloxane
- 5 silicone oil A having the specifications given above in Example 1;
- 7.2 kg/hour of the hydroxylated organopolysiloxane resin B having the specifications given above in Example 1;
- 10 - 7.2 kg/hour of α,ω -di(trimethylsiloxyl)polydimethylsiloxane oil F with a viscosity of 100 mPa·s at 25°C having the mean formula:



approximately 70

- 15 - 0.3 kg/hour of the 4% by weight solution of lithium hydroxide ($\text{LiOH} \cdot \text{H}_2\text{O}$) in methanol which is described above in Example 1; and
- 2.4 kg/hour of vinyltrimethoxysilane C.

Stage 2: 9 kg/hour of the fumed silica G

20 having the specifications given above in Example 1 are introduced into zone No. 2 of the extruder, the introduction being carried out at ambient temperature (23°C), and then the n-butyl titanate H1 is introduced into zone No. 5 of the extruder at the rate of

1 kg/hour, this feeding again being carried out at ambient temperature (23°C).

Stage 3: the material present in the extruder is subsequently subjected, in zone No. 7 of the device, to a devolatilization operation carried out under a pressure of the order of 66×10^2 Pa. The outlet throughput of the extruder is 80 kg/hour and the temperature of the composition which emerges from the extruder is 80°C.

The various properties appear in the following Table 1.

TABLE 1

Properties	Example 1	Example 2
Tack-free time (min)	85	120
Yellowing index	4.0	4.0
Transparency index	12.5	14
Adhesion to PVC		
PVC u (1)	+	+
PVC Kommerling (2)	+	+
PVC Rehau (3)	+	+
PVC Vêka (4)	+	+
PVC Anglian (5)	+	+
SAH (2 mm)	21	17
SAH (6 mm)	22	20
T/S (2 mm) in MPa	2.4	2.4
A/B (2 mm) in %	820	950
M 100 (2 mm) in MPa	0.46	0.35

(1) PVC sold by Interplast Industrie under the name PVC u.

(2) PVC sold by Kommerling under the name PVC Kommerling.

(3) PVC sold by Rehau under the name PVC Rehau.

(4) PVC sold by Vêka under the name PVC Vêka.

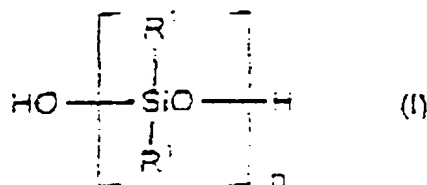
(5) PVC sold by Anglian under the name PVC Anglian.

CLAIMS

1. Single-component organopolysiloxane compositions which are stable on storage in the absence of moisture and which crosslink to translucent and adherent elastomers in the presence of moisture, characterized in that they are capable of being obtained by carrying out, in a single closed reactor with stirring, operating according to a batchwise mode or a continuous mode, successive stages 1 to 3 defined below:

• stage 1: functionalization stage, during which:

(i) at least one reactive linear diorganopolysiloxane A comprising a hydroxyl group at each chain end, of formula:



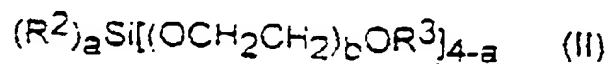
in which:

- the R^1 substituents, which are identical or different, each represent an aliphatic, cyclanic or aromatic, saturated or unsaturated, substituted or unsubstituted, C_1 to C_{13} monovalent hydrocarbonaceous radical;
- n has a value sufficient to confer, on the diorganopolysiloxanes of formula (I), a

dynamic viscosity at 25°C ranging from 1 000 to 1 000 000 mPa·s;

(2i) and at least one hydroxylated organopolysiloxane resin B exhibiting, in its structure, at least two different units chosen from those of formulae $(R^1)_3SiO_{1/2}$ (M unit), $(R^1)_2SiO_{2/2}$ (D unit), $R^1SiO_{3/2}$ (T unit) and SiO_2 (Q unit), at least one of these units being a T or Q unit and the R^1 radicals, which are identical or different, having the meanings given above with respect to the formula (I), the said resin having a content by weight of hydroxyl group ranging from 0.1 to 10%;

(3i) are reacted with at least one polyalkoxysilane C of formula:



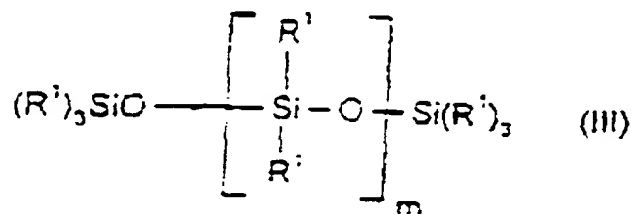
in which:

- the R^2 substituent represents an aliphatic, cyclanic or aromatic, saturated or unsaturated, substituted or unsubstituted, C_1 to C_{13} monovalent hydrocarbonaceous radical;
- the R^3 symbols, which are identical or different, each represent a linear or branched C_1 to C_8 alkyl radical;
- a is zero or 1;
- b represents zero or 1;

(4i) the reaction of (i) and (2i) with (3i) being carried out in the presence of a catalytically effective amount of a functionalization catalyst D, with the exception of the use of an organic titanium derivative;

(5i) it being possible for the reaction medium of stage 1 additionally to comprise:

- + at least one aliphatic C₁ to C₃ alcohol E; and/or
- + at least one nonreactive linear diorganopolysiloxane F of formula:



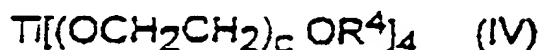
in which:

- the R¹ substituents, which are identical or different, have the same meanings as those given above for the reactive diorganopolysiloxane A of formula (I);
- m has a value sufficient to confer, on the polymers of formula (III), a dynamic viscosity at 25°C ranging from 10 to 200 000 mPa·s;
- stage 2: blending (or compounding) stage, during which:

(6i) an inorganic filler G based on amorphous silica
in the form of a solid;

(7i) an effective amount of a curing catalyst H
comprising at least one organic titanium
5 derivative chosen from the group consisting of:

+ H1 monomers of formula:



in which:

- the R^4 substituents, which are identical or
10 different, each represent a linear or
branched C_1 to C_{12} alkyl radical;
- c represents zero, 1 or 2;
- with the conditions according to which, when
the c symbol represents zero, the R^4 alkyl
15 radical has from 2 to 12 carbon atoms and,
when the c symbol represents 1 or 2, the R^4
alkyl radical has from 1 to 4 carbon atoms;
- + H2 polymers resulting from the partial
hydrolysis of the monomers of formula (IV) in
20 which the R^4 symbol has the abovementioned
meaning with the c symbol represent zero;

(8i) optionally at least one nonreactive linear
diorganopolysiloxane F corresponding to the
formula (III) mentioned above; and

25 (9i) optionally at least one auxiliary agent I known
to a person skilled in the art, which is
generally chosen, when it is needed, according

to the applications in which the compositions
according to the present invention are employed;
are introduced in any order into the
functionalization medium of stage 1, which is kept
5 stirred;

- stage 3: finishing stage, during which the base blend obtained, kept stirred, is subjected to a devolatilization operation carried out under a pressure below atmospheric pressure.

10 2. Compositions according to claim 1, characterized in that the following are used to prepare the single-component organopolysiloxane compositions, on the basis of 100 parts by weight of hydroxylated linear diorganopolysiloxane(s) A:

- 15 - from 3 to 30 parts of hydroxylated resin(s) B,
- from 2 to 15 parts of polyalkoxysilane(s) C,
- a catalytically effective amount of functionalization catalyst D,
- from 0 to 2 parts of alcohol(s) E,
20 - from 0 to 30 parts of nonreactive linear diorganopolysiloxane(s) F,
- from 2 to 40 parts of siliceous filler G,
- from 0.3 to 5 parts of organic titanium derivative(s) H, and
25 - from 0 to 20 parts of auxiliary agent(s) I.

3. Compositions according to claim 1 or 2, characterized in that the R¹ substituents of the

7. Compositions according to claim 6, characterized in that the polyalkoxysilanes C of formula (II) are chosen from: $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{CH}_3\text{Si}(\text{OCH}_3)_3$, $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$, $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{OCH}_3)$, $(\text{CH}_2=\text{CH})\text{Si}(\text{OCH}_3)_3$ and
5 $(\text{CH}_2=\text{CH})\text{Si}(\text{OC}_2\text{H}_5)_3$.

8. Compositions according to any one of claims 1 to 6, characterized in that use is made, as functionalization catalyst D, of lithium hydroxide of formula LiOH or $\text{LiOH}\cdot\text{H}_2\text{O}$.

10 9. Compositions according to claim 8, characterized in that use is made of 0.005 to 0.5 mol of lithium hydroxide per 1 mol of silanol groups contributed, first, by the hydroxylated polymer(s) A and, secondly, by the hydroxylated resin(s) B.

15 10. Compositions according to any one of claims 1 to 9, characterized in that the inorganic filler G is chosen from treated or untreated precipitated silicas in the powder form, treated or untreated fumed silicas in the powder form, or their
20 mixtures, the BET specific surface areas of these silicas being greater than $40 \text{ m}^2/\text{g}$.

11. Compositions according to any one of claims 1 to 10, characterized in that the curing catalyst H is chosen from organic titanium derivatives,
25 including the H1 monomers of formula (IV) and the H2 polymers resulting from the partial hydrolysis of the H1 monomers, in the structure of which the R^4 symbol is